Metal concentration versus water discharge during single hydrologic events in a small stream (NW Spain)

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1. Abstract

Metal data is present for four rainfall events in a small stream draining an agroforestry catchment in the NW Spain. Aluminum, iron, manganese, copper and zinc, in particulate and dissolved forms were studied. The relationships between metals concentrations (particulate and dissolved fraction) and stream discharge were investigated. In general, the particulate fraction in the events is high, accounting for over 90% of Al, Fe and Mn total and over 70% of the total Cu, except in one event. The particulate fractions of Al, Mn and Fe show significant and positive correlation with flow and suspended solids. Variations in the concentration of metals during rainfall events often result in a hysteresis effect with different concentration during the rising and falling limb of the hydrograph. The general trend of particulate metals is to generate clockwise hysteretic loops, while for dissolved metals are also important anticlockwise hysteresis.

2. Introduction

Soils play a major role in food production and are usually the interface between human activities and other parts of the environment. Soils not only serve as sources for certain metals but also function as sinks for metal contaminants (Alloway, 1995). Excess metal levels in soils and waters may pose a health risk to humans and to the environment. Metals are easily influenced by environmental factors such as surface runoff, groundwater, dissolution from sediment, deposition from the atmosphere and anthropogenic pollutants. Hence, trace elements may be sensitive indicators for monitoring changes in the water environment. At cachtment scale the transport of metals fron soil may result in increased contents of metals in the ground water or surface water (Taboada et al., 2002; Xue et al., 2003). Metals discharged into aquatic systems are mostly adsorbed on suspended particles and fine grained riverine sediments, but are also in dissolved form. Distribution, mobility and bioavailability of heavy metals in rivers do not simply depend on total concentrations but, critically, on their chemical and physical associations and on transformation processes they undergo. Gradually, contaminant potentials are formed in the sediments, from which under changing chemical conditions heavy metals can be mobilized (Hong et al., 1991). Understanding possible mobilization and transformation effects of metals bound to sediments requires detailed studies of release mechanisms and how they are affected by hydrodynamic and biogeochemical processes (Calmano et al., 2005).

Hydrological processes have been shown to exert a major control in several small and large rivers (Bhangu and Whitfield, 1997, Sherrell and Ross, 1999, Neal et al., 2000). Correlations of metal concentrations with fundamental variables including discharge may be used to infer potential mechanisms controlling trace metal fluxes. Much metal load is transported during rain events. Xue et al. (2000), studying the transport of Cu and Zn in a small agricultural catchment, showed that one single rain event can contribute almost one third of the yearly Cu and Zn loads. Therefore, transport of metals from rural catchments to fluvial systems merits further attention due to their potential impact on ecological health of surface water systems.

The aim of this study is to characterize the behaviour heavy metals (Al, Fe, Mn, Cu and Zn) in a small stream draining an agroforestry catchment in the temperate humid area of Spain during four rainfall events. The relationships between metals concentrations (particulate and dissolved fraction) and stream discharge were investigated.

3. Methods

The studied catchment and stream are located in Galicia, NW Spain. The Corbeira catchments covers and area of 16 km^2. It is part of Mero catchment which is dominates by schist and the soil texture is silt and silt-loam. Predominant soils are Umbrisol and Cambisol. Elevation ranges from 60 to 474 m and mean slope is next to 20%.The climate in this area is humid temperate and mean rainfall is about 1024 mm (1985-2005), mostly concentrated in autumn and winter.

The catchment is mainly covered by forest (65%). Agricultural is the second most common land used. Agriculture is mainly grassland, pasture and maize, but also some fields are used for winter cereals, potatoes and orchard. In addition some fields were bare after maize harvest, although the most of the catchment has a good vegetation cover during the year. Soil management is conventional. This catchment lacks industrial activity, so possible sources leading to the modification of the natural composition of waters are associated with the agricultural activity and the spills from the small dispersed population group, directly or indirectly, through infiltrations from septic tanks.

We used an ISCO 6712 automatic sampler fitted with a pressure sensor to monitor discharge stages at the catchment outlet. The sampler was programmed to collect water sampler during rainfall events at irregular intervals. In the laboratory, water samples for total metal analysis were digested with HCl-HNO_3 in a microware. Water samples for dissolved metals were filtered through 0.45 μm and acidified with HNO_3 to pH <2. Metals were measured by ICP-MS. The particulate fraction, i.e. the component specifically associated with the suspended sediment, was calculated as the difference between the total and dissolved fraction. When measurements were below the detection limits, the concentration was considered to be half the detection limit concentration.

4. Results

Table 1 shows characteristics of the events and the table 2 a statistical summary of metals (particulate and dissolved) concentrations for each event. Mean concentration was calculated as discharge weighted values. There were substantial variations concentrations during events, in general more pronounced for the particulate than the dissolved fraction (Table 2). The particulate fraction in the events is high, accounting for over 90% of Al, Fe and Mn total and over 70% of the total Cu, except in the event 4, in which represents 51%. However, the dissolved Zn predominates in the events 1 and 2, while in events 3 and 4 dominated the particulate. The increase in the particulate metals concentrations during the events related to sediment delivery from soil surface. Data show variability of peak particulate metals between events. These differences are probably due to the event characteristics and time of the year, among others. The highest concentrations were obtained in the event 1, which took place in the wet season under conditions that trigger sediment sources.

Table 1 Event characteristics

	Total rainfall (cm)	Rainfall duration (h)	Range discharge (m^3/s)
1: 28-30/12/2004	2.2	10	0.17 - 0.58
2: 26-28/03/2005	1.9	25	0.28 - 0.48
3: 02/05/2005	0.4	2	0.32 - 0.38
4: 19-20/10/2005	4.7	29	0.05 - 0.37

Table 2 Minimum, mean and maximum concentration of particulate and dissolved metals (μg/L)

		Alp	**Ald**	**Fep**	**Fed**	**Mnp**	**Mnd**	**Cup**	**Cud**	**Znp**	**Znd**
1	Min	382.18	8.73	426.70	25.12	18446.00	2.08	0.21	0.30	0.50	1.50
	Mean	3321.98	26.05	4928.03	62.36	173.60	4.20	3.63	0.56	6.03	7.20
	Max	11233.30	54.00	16588.38	107.20	548.99	10.29	12.27	1.07	36.34	14.50
2	Min	144.57	10.40	274.89	45.11	4.98	0.59	0.05	0.28	0.10	1.54
	Mean	1673.14	25.36	1663.81	76.45	67.10	1.50	1.38	0.56	1.92	4.17
	Max	3732.91	38.50	4227.35	109.00	172.79	4.12	3.14	0.84	10.62	12.70
3	Min	536.61	11.26	578.65	32.92	20.43	0.18	1.30	0.35	0.74	1.04
	Mean	867.02	14.09	901.08	36.36	28.70	0.18	3.98	0.35	7.74	1.36
	Max	1405.78	16.19	1408.20	37.22	40.76	0.22	7.80	0.44	24.44	1.52
4	Min	35.85	9.77	72.50	61.90	4.03	0.36	0.04	0.43	0.06	0.38
	Mean	903.63	29.51	1155.79	107.03	47.15	0.70	0.89	0.85	4.73	2.24
	Max	2989.02	40.54	3831.50	149.30	152.38	0.85	2.73	1.06	9.19	5.39

All particulate metals show significant and positive correlation with SS (data not shown), except Cu and Zn in event 3. The positive correlation of particulate metals with SS was also reported by many authors (Neal et al, 1997, Rodríguez et al., 2005) and suggests that these constituents play a major role in the transport of metal ions. Moreover significant and positive relationship was obtained with discharge, except for Cu in event 3, and Zn in events 2 and 3. In the latter the relationship was negative. For the dissolved fraction, the relationships with discharge are more diverse.

In spite that there is a significant increase in particulate metals concentrations during storm flow, however the relationships between stream discharge and metal concentration are not straightforward. Examples of discharge / concentrations rating plots are given in figure 1, which shows clockwise and anticlockwise hysteretic loops. The general trend of particulate metals is to generate clockwise hysteretic loops (with highest concentrations recorded on the rising limb of the hydrograph), which suggest early mobilization from near sources to the stream.

In dissolved metals the increase and decrease of concentrations typically occur more gradually than in the particulate. In some cases, the peak concentrations recorded on the falling limb of the hydrograph (anticlockwise or negative hysteresis), which suggest a greater transport of these elements in the subsurface flow; while in others the peak concentrations occurred prior the discharge peak (clockwise or positive hysteresis). Further work is required to identify the relative roles of hydrological and in situ geochemical processes versus the distribution and composition of source material, on these patterns.

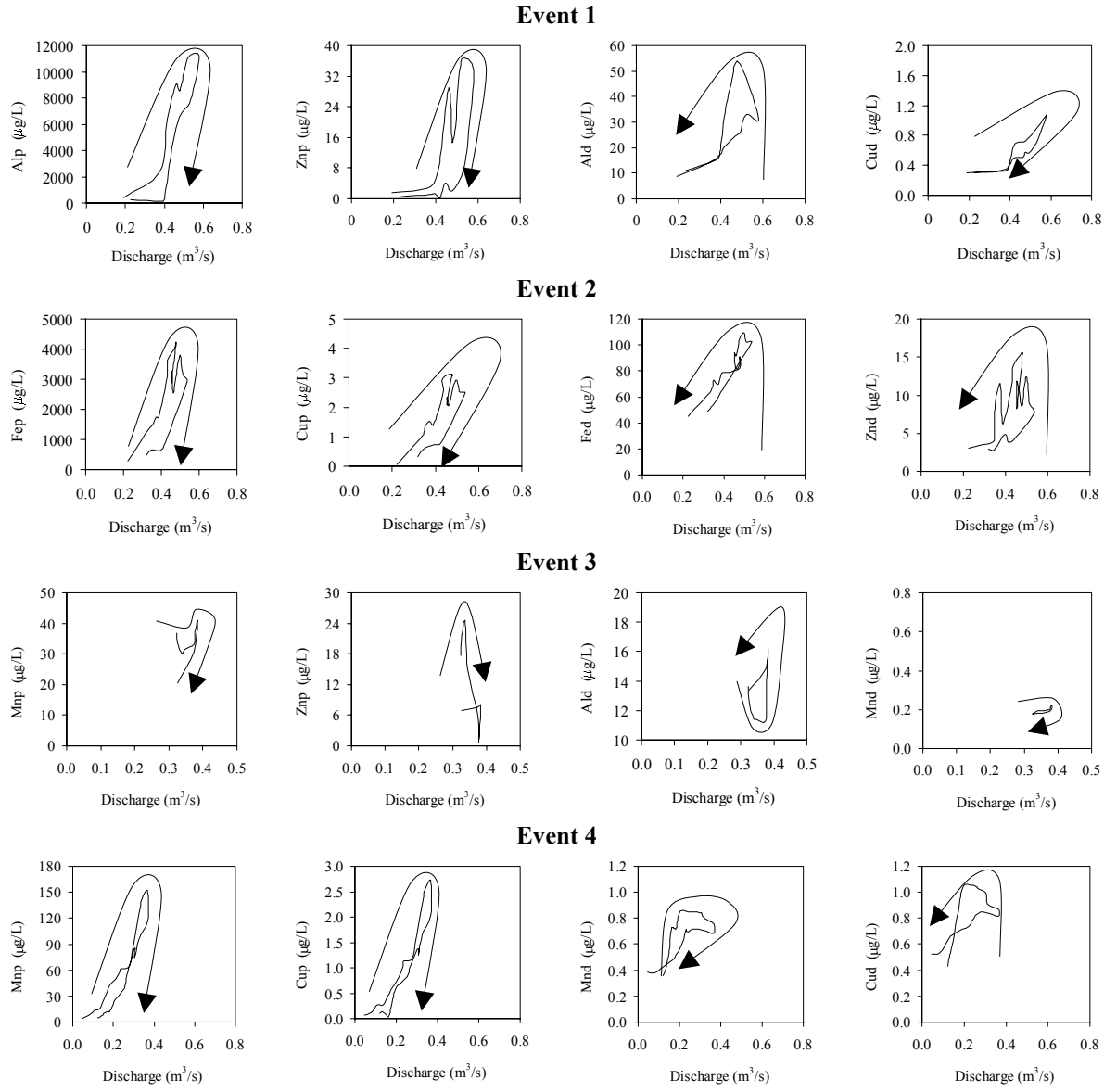

Figure 1 Examples of some discharge /concentrations hysteretic rating plot for some metals

4. Conclusions

The results of this work show that metal concentrations varied widely among and during single rainfall events. The metals were predominantly associated to particles. This confirms the importance of suspended sediment as a vehicle for transportation of metals from the soil to the stream.

This study demonstrates that the direction of hysteresis in the metals concentration/river discharge relationship is predominantly clockwise for particulate metals. This has been attributed to early mobilization from near sources to the stream. However, the dissolved metals showed in some cases anticlockwise loops, which could be linked to the greater transport of these in the subsurface flow.

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